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POLYESTER COMPOSITE MATERIAL AND MANUFACTURING METHOD THEREOF

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Claims

1. A polyester composite material, characterized by the following facts: the polyester composite material contains a thermoplastic aromatic polyester, a layer clay mineral with bonded organic onium ions, and a compatibilizer; under the affinity effect of the compatibilizer, the layer clay mineral with bonded organic onium ions is dispersed uniformly in the thermoplastic aromatic polyester and crosslinked by the molecular chains of the thermoplastic aromatic polyester.

2. The polyester composite material described in Claim 1, characterized by the fact that the aforementioned crosslinked structure is supported by the entanglement between the organic onium ions bonded to the layer clay mineral and the molecular chains of the thermoplastic aromatic polyester.

3. A manufacturing method for polyester composite material, characterized by having the following steps: a step in which a layer clay mineral is reacted with an organic onium salt to form an organic clay compound material with organic onium ions bonded to the layer clay mineral, a step in which the aforementioned organic clay compound material is mixed with an aromatic polyester monomer in the presence of a compatibilizer, and a step in which the aforementioned aromatic polyester is polymerized.

4. A manufacturing method for polyester composite material, characterized by having a step in which a layer clay mineral is reacted with an organic onium salt to form an organic clay compound material with organic onium ions bonded to the layer clay mineral, and a step in which the aforementioned organic clay compound material is mixed and/or kneaded with an aromatic polyester in the presence of a compatibilizer.

Detailed explanation of the invention

Industrial application field

The present invention pertains to a polyester composite material and its manufacturing method. More specifically, the present invention pertains to a composite material of thermoplastic aromatic polyester, in which a layer clay mineral is uniformly dispersed and bonded, and to its manufacturing method.

Prior art and problems

Polyethylene terephthalate, polybutylene terephthalate, and other thermoplastic aromatic polyesters (simply referred to as polyester hereinafter) have excellent mechanical strength (such as elastic modulus), electric insulation property, chemical resistance, processibility, and surface appearance (such as smoothness of the surface). Therefore, they have been widely used as the so-called engineering plastics or as film materials.

These polyesters, however, are inferior in rigidity (such as resistance to scratches on the surface), heat resistance, and water resistance (hydrolysis resistance). As a result, application of these polyesters is limited for products in which surface scratches should be prevented, products around automobile engines and other products used in high-temperature environments, and products used in places with high humidity.

As a method for solving this problem, for example, the polyesters are kneaded with substances obtained by processing clay or other inorganic fillers with organic silanes (Japanese Kokai Patent Application Nos. Sho 51[1976]-24653 and Sho 51[1986]-24654, etc.). In this conventional technology, however, since no pretreatment is carried out to separate the various unit layers of the layer clay mineral from each other, in a process of forming yarns, films, etc., clogging of the filter, breakage of yarns, or damage of the films might occur due to the huge particles of the clay mineral (block-shaped particles formed with many unit layers laminated and adhered to each other). In particular, fish eyes (small defects in the shape of a fish eye), dropout for magnetic tapes (omission of magnetic recording), and other problems will occur with polyethylene terephthalate. Also, in this conventional technology, the layer clay mineral is neither separated for each unit layer in the material nor uniformly dispersed, and thus the layer clay mineral almost makes no contribution to formation of the high-order steric structure (such as crosslinked structure) in the material. Therefore, the rigidity, heat resistance, and water resistance cannot be well improved.

On the other hand, in the polyamide resin field, for the composite material disclosed in Japanese Patent Application No. 60[1985]-217396 (Japanese Kokai Patent Application No. Sho 62[1987]-74957) applied by the present applicant, the layer clay mineral is pretreated with a swelling agent (organic onium ions), and the pretreated layer clay mineral is mixed with

polyamide monomer to provide a polyamide clay composite material. In this composite material, the layer clay mineral pretreated with the swelling agent is separated for each unit layer and is uniformly dispersed in the composite material, and the molecular chains of the polyamide form a crosslinked structure via the layer clay mineral. Consequently, the rigidity, heat resistance, and water resistance of the polyamide resin are significantly improved.

If the technical measures taken for the polyamide clay composite material can be applied effectively to polyester, it is possible to obtain a composite material free of the problems of the aforementioned various conventional technologies. However, polyester is different from polyamide due to the structural characteristics, such as the fact that polyester has ester bonds or a benzene ring in the molecular chain. As a result, the affinity of polyester with the layer clay mineral is not high enough. Consequently, even if the layer clay mineral that has been simply pretreated with a swelling agent is added into the polyester, the layer clay mineral cannot be uniformly dispersed, and it is unable to obtain a polyester composite material with the desired characteristics.

Objective of the invention

A purpose of the present invention is to provide a polyester clay composite material in which a layer clay mineral is uniformly dispersed and contributes to formation of the crosslinked structure of the polyester molecular chains. Another purpose of the present invention is to provide a polyester composite material that can be used as excellent film material, etc., with good balance in mechanical properties, thermal properties, and water resistance which is absent in the conventional technology. Yet another purpose of the present invention is to provide a method for manufacturing the aforementioned polyester composite material.

Explanation of the invention

Constitution of the first invention

The first invention for realizing the aforementioned purposes provides a polyester composite material characterized by the following facts: the polyester composite material contains a thermoplastic aromatic polyester, a layer clay mineral with bonded organic onium ions, and a compatibilizer; under the affinity effect of the compatibilizer, the layer clay mineral with bonded organic onium ions is dispersed uniformly in the thermoplastic aromatic polyester and crosslinked by the molecular chains of the thermoplastic aromatic polyester.

Function and effect of the first invention

The composite material of the present invention has excellent total balance among mechanical properties, thermal properties, and water resistance. It can also be used as excellent film-forming material, etc.

In the composite material of the present invention, since the compatibilizer has contact with both the layer clay mineral with organic onium ions and the polyester to improve the affinity between them, the molecular chains of the polyester are entangled with the aforementioned organic onium ions.

As a result, the molecular chains of the polyester are crosslinked with the layer clay mineral with organic onium ions and become difficult to be mechanically or thermally deformed. Consequently, excellent tensile strength, elastic modulus, and other mechanical properties, as well as excellent softening temperature, high-temperature strength, and other thermal properties can be realized. Because of the affinity improving effect of the aforementioned compatibilizer, the layer clay mineral can be dispersed uniformly in the composite material. Therefore, the layer clay mineral becomes a water barrier to reduce the water absorption. Also, since the size of the layer clay mineral is usually as small as 1000 Å, the characteristics of the material will not be affected adversely when it is used as a film-forming material.

Constitution of the second invention

In the following, the second invention which further details the first invention will be explained.

In the second invention, the thermoplastic aromatic polyester disclosed in the aforementioned first invention is a thermoplastic saturated or unsaturated polyester containing aromatic rings. It is a polymer or copolymer obtained from a polycondensation reaction between an acid component mainly composed of an aromatic dicarboxylic acid (or its ester derivative) and a diol component.

Examples of the aromatic dicarboxylic acids that can be used here include terephthalic acid, isophthalic acid, 2,5-naphthalenedicarboxylic acid, 2,6-naphthalenedicarboxylic acid, 4,4'-diphenyldicarboxylic acid, 4,4'-diphenyl ether dicarboxylic acid, 4,4'-diphenylmethanedicarboxylic acid, 4,4'-diphenylsulfonedicarboxylic acid, 4,4'-diphenylisopropylidenedicarboxylic acid, etc., among which terephthalic acid is preferred.

These aromatic dicarboxylic acids can also be used as mixtures of two or more types. These aromatic dicarboxylic acids can also be used as a mixture with one or several types of aliphatic dicarboxylic acids, such as adipic acid, azelaic acid, dodecanedioic acid, and sebacic acid, as well as alicyclic dicarboxylic acids, such as cyclohexanedicarboxylic acid, in such a small amount that the characteristics of the polyester component will not be affected adversely.

Examples of the diol components that can be used include ethylene glycol, propylene glycol, butylene glycol, hexylene glycol, neopentyl glycol, and other aliphatic diols, 1,4-cyclohexanedimethanol and other alicyclic diols, xylylene diglycol, bis(4,4'-dihydroxyphenyl)ethane, and other aromatic diols, as well as their mixtures. It is also possible to copolymerize one or several types of long-chain diols with a molecular weight in the range of 400-6000, such as polyethylene glycol and polytetramethylene glycol, in such a small amount that the polyester composite material will not be gummed. Examples of the polyesters of the present invention include polyethylene terephthalate, polybutylene terephthalate, polybutylene naphthalate, as well as polyethylene isophthalate/terephthalate copolymer, polybutylene terephthalate/isophthalate copolymer, polybutylene terephthalate/decanedicarboxylate copolymer, and other copolymerized polyesters. Among them, polyethylene terephthalate and polybutylene terephthalate are preferred.

The layer clay mineral with bonded organic onium ions used for the composite material of the present invention is obtained by substituting the inorganic ions of a layer clay mineral that has cation exchangeability with organic onium ions. When the inorganic ions in the clay mineral are substituted with organic onium ions, the interlayer space of the clay mineral can be expanded.

Organic onium ions are represented by X^+-R-Y . X^+ is an ammonium ion, pyridinium ion, phosphonium ion, or sulfonium ion. R is an alkyl group, phenyl group, alkylene group, or other organic compound group. Y is a hydrogen, hydroxyl group, amino group, carboxyl group, nitro group, sulfone group, or their derivatives. Among them, 4-aminododecanoic acid ions, 6-aminocaproic acid ions, 1,2-aminododecanoic acid ions, and 18-aminooctadecanoic acid ions are preferred.

Examples of the layer clay minerals that can be used include montmorillonite, saponite, beidellite, hectorite, steibunsite [transliteration], and other smectite-type clay minerals, vermiculite, halloysite, and swelling mica. Both natural and synthetic layer clay minerals can be used.

It is preferred to pulverize the layer clay mineral with a mixer, ball mill, vibratory mill, pin mill, jet mill, or pulverizer to obtain the desired shape and size.

The compatibilizer used in the present invention is a compound that has an affinity for both the polyester and the layer clay mineral with bonded organic onium ions. Examples of the compatibilizer that can be used include (a) β -propyllactone, γ -butyrolactone, δ -valerolactone, ϵ -caprolactone, and other lactones and their polymers, (b) β -propyllactam, γ -butyrolactam, δ -valerolactam, ϵ -caprolactam, and other lactams and their polymers, (c) oligomers of the aforementioned thermoplastic aromatic polyesters, (d) γ -glycidoxypropyltrimethoxysilane, β -(3,4-epoxycyclohexyl)ethyltrimethoxysilane, and other silane-based coupling agents, as well

as tri(stearyl)titanate isopropoxide, tri(dodecylbenzenesulfonyl)titanate isopropoxide, and other titanate-based coupling agents. These compatibilizers can be used either alone or as a mixture of several types.

In the present invention, "dispersion" of the layer clay mineral means that the layer clay mineral is uniformly dispersed with the interlayer distance kept at 20 Å or larger on average. Here, the interlayer distance means the distance between the gravity centers of the plates of the laminar silicate salt. Uniform dispersion refers to a state in which each of the unit layers of the laminar silicate salt or multilayer laminate of 5 or less layers on average is dispersed in parallel and/or randomly with 50% or more, preferably, 70% or more of the layers having no lumps.

The composite material of the present invention can be adjusted to have desired characteristics or properties by properly mixing polycarbonate, polycapromide (nylon 6), polyhexamethylene adipamide (nylon 66), and other polyamide resins, polystyrene (PS), styrene/acrylonitrile copolymer (SAN), polymethyl methacrylate (PMMA), and other vinyl-based polymers, methacrylic acid-butadiene-styrene tertiary copolymer (MBS) resin, ABS resin, polyethylene, polypropylene, ethylene/propylene copolymer, and other olefin-based resins as needed in addition to the thermoplastic aromatic polyester, the layer clay mineral with bonded organic onium ions, and the compatibilizer. If necessary, it is also possible to add pigments or dyes, glass fibers, metal fibers, metal flakes, carbon fibers, or other reinforcing materials or fillers, thermal stabilizing agents, antioxidants, UV absorbers, photostabilizing agents, lubricants, plasticizers, antistatic agents, and flame retardants, etc.

The composite material of the present invention can be formed by means of direct injection molding or molding carried out under heating and pressurization. It is also possible to carry out the polymerizing reaction in a prescribed mold to obtain the molding product.

If the amount of the polyester is 50 parts by weight or less and the amount of the compatibilizer is 30 parts by weight or more, since the amount of the polyester matrix in the composite material is small, the excellent mechanical properties, electric properties, chemical resistance, and processibility of the polyester will be deteriorated. If the amount of the layer clay mineral with bonded organic onium ions is 50 parts by weight or more, since the amount of the matrix component is small, the uniform dispersion of the layer clay mineral with bonded organic onium ions will be affected adversely, and the obtained material becomes brittle.

If the amount of the polyester is 99 parts by weight or more and the amount of the layer clay mineral with bonded organic onium ions is 0.1 part by weight or less, since the amount of the layer clay mineral with bonded organic onium salt is too small, the influence on the polyester matrix is too low to achieve any improvement.

There is no special limitation on the proportions of the organic onium ions and layer clay mineral in the layer clay mineral with bonded organic onium ions.

The layer clay mineral is a clay mineral that has a cation-exchange capacity of 50-300 milliequivalents/100 g and a large contact area with the monomer to be reacted with.

In this case, the reason that the cation-exchange capacity is limited to the range of 50-300 milliequivalents/100 g is because if the capacity exceeds 300 milliequivalents/100 g, it becomes difficult to obtain the desired composite material of the present invention since the interlayer bonding force of the layer clay mineral is increased. On the other hand, if the capacity is lower than 50 milliequivalents/100 g, exchange adsorption depending on the organic onium ions cannot be well carried out, making it difficult to obtain the desired composite material.

For the polyester disclosed in the present invention, the intrinsic viscosity measured at 30°C in a solution of phenol/tetrachloroethane = 6/4 (weight ratio) is preferred to be in the range of 0.5-2.0. If the intrinsic viscosity is less than 0.5, the impact strength of the obtained molding product is low. If it is larger than 2.0, the gloss on the surface of the molding product is poor.

Function/effect of the second invention

Although the function and effect of the second invention are basically the same as those of the aforementioned first invention, with the amounts measured in parts by weight of the thermoplastic aromatic polyester, the layer clay mineral with bonded organic onium ions, and the compatibilizer contained in the aforementioned respective ranges, a practical polyester composite material that has excellent total balance among physical properties, thermal properties, and water resistance and can be used as an excellent film material can be obtained.

Constitution of the third invention

The constitution of the third invention for providing a useful method for manufacturing the aforementioned polyester composite material has the following steps: a step in which a layer clay mineral is reacted with an organic onium salt to form an organic clay compound material with organic onium ions bonded to the layer clay mineral, a step in which the aforementioned compound clay compound material is mixed with an aromatic polyester monomer in the presence of a compatibilizer, and a step in which the aforementioned aromatic polyester is polymerized.

In this case, there is no special limitation on the method for synthesizing the layer clay mineral with bonded organic onium ions. The layer clay mineral can be synthesized using various methods. For example, it can be synthesized by mixing a layer clay mineral and organic onium ions on one or several types of solvents selected from water, methanol, ethanol, propanol, isopropanol, ethylene glycol, 1,4-butanediol, glycerol, etc. When the layer clay mineral used is montmorillonite, it is desired to use one or several types of solvents selected from water, methanol, and ethanol. The composite material is usually prepared after the solvents are removed

in advance (dry method). When solvents other than water are used, it is also possible to use the layer clay mineral directly to form the composite material without removing the solvents (wet method) in consideration of the fact that the solvents do not accelerate hydrolysis of the polyester, the fact that work and energy can be saved without carrying out the operation for removing the solvents, and the fact that it is easy to realize large uniform dispersibility for the polyester when using the original organic clay compound material containing the solvents.

The method of the present invention can be carried out by mixing or melt kneading the compatibilizer after the compatibilizer aromatic polyester is polymerized in the presence of the layer clay mineral with bonded organic onium ions or by polymerizing the compatibilizer aromatic polyester in the presence of the substance obtained by mixing or melt kneading the compatibilizer and the layer clay mineral with bonded organic onium ions.

Function and effect of the third invention

The polyester composite material disclosed in said first or second invention can be manufactured according to the present invention. That is, as described in the aforementioned section of function and effects of the first invention, when the organic clay compound material and the polyester that have no affinity between them are brought into contact with each other in the presence of the compatibilizer, a polyester composite material in which the layer clay mineral is uniformly dispersed and the molecular chains of the polyester are crosslinked via the layer clay mineral can be obtained.

Also, in the present invention, since the polyester monomer is polymerized in a mixed state with the organic clay compound material, the polymerizing reaction is carried out within the layer clay mineral. Therefore, the dispersibility of the layer clay mineral in the polyester composite material is especially good.

Constitution of the fourth invention

The constitution of the fourth invention for providing a useful method for manufacturing the aforementioned polyester composite material has a step in which a layer clay mineral is reacted with an organic onium salt to form an organic clay compound material with organic onium ions bonded to the layer clay mineral, and a step in which the aforementioned organic clay compound material is mixed and/or kneaded with an aromatic polyester in the presence of a compatibilizer.

As far as the composite material manufacturing method disclosed in the present invention is concerned, the thermoplastic aromatic polyester, the layer clay mineral containing organic onium ions, and the compatibilizer can be first well mixed with a powerful stirrer and then melt kneaded with a monoaxial or biaxial extruder. It is also possible to carry out melt kneading after

mixing the thermoplastic aromatic polyester with the substance obtained by mixing or melt kneading the compatibilizer and the layer clay mineral with bonded organic onium ions.

Function and effect of the fourth invention

According to the present invention, the polyester composite material disclosed in said first or second invention can be manufactured with the same operation as described in the case of said third invention.

Also, in the present invention, since the polymerized polyester is mixed and/or melt kneaded with the organic clay compound material, the switching loss can be reduced when switching the polymerized materials. This is considered an advantage for the manufacturing process.

Application examples

In the following, the application examples of the present invention will be explained.

The tensile elastic modulus for evaluating the rigidity and the thermal deformation temperature for evaluating the heat resistance were measured according to ASTM.

To evaluate the water resistance, the weight variation rate of a tension test piece was measured after it was immersed in boiling water with a temperature of 100°C for 30 min.

The film formability was evaluated as O if film formation was actually possible and as X if film formation was impossible.

Application Example 1

100 g of montmorillonite produced in Yamagata Ken (cation-exchange capacity: 119 milliequivalents/100 g) were dispersed in 3 L water, followed by adding 51.2 g 12-aminododecanoic acid and 24.1 g of concentrated hydrochloric acid (concentration: 36%). The mixture was stirred at room temperature for 60 min. After being well rinsed, the mixture was filtered under reduced pressure by using a Buchner funnel to obtain a water-containing compound material. The water-containing compound material was subjected to freeze-drying to synthesize a montmorillonite (compound material A) containing ammonium ions of 12-aminododecanoic acid.

25 g of the obtained compound material A, 42 g ϵ -caprolactone polymer, and 933 g of a polybutylene terephthalate (referred to as PBT hereinafter) resin ("Juranex" 2000, product of Polyplastics K.K.) were blended with a Henschel mixer, followed by extrusion/molding performed at 250°C. The properties of the obtained molding product were evaluated.

Application Example 2

After 125 g of said compound material A, 75 g ϵ -caprolactone polymer, and 800 g PBT resin ("Juranex" 2000, product of Polyplastics K.K.) were blended with a Henschel mixer, the obtained mixture was processed in the same way as described in Application Example 1. The properties of the obtained molding product were evaluated.

Application Example 3

After 25 g of said compound material A, 15 g of a polybutylene terephthalate oligomer (molecular weight: about 1000) that was synthesized separately, and 960 g PBT resin ("Juranex" 2000, product of Polyplastics K.K.) were blended with a Henschel mixer, the obtained mixture was processed in the same way as described in Application Example 1. The properties of the obtained molding product were evaluated.

Application Example 4

100 g montmorillonite produced in Yamagata Ken (cation-exchange capacity: 119 milliequivalents/100 g) were dispersed in 3 L water, followed by adding 30.8 g 6-aminocaproic acid and 24.1 g of concentrated hydrochloric acid (concentration: 36%). The mixture was stirred at room temperature for 60 min. After being well rinsed, the mixture was filtered under reduced pressure using a Buchner funnel to obtain a water-containing compound material. The water-containing compound material was subjected to freeze-drying to synthesize a montmorillonite (compound material B) containing ammonium ions of 6-aminocaproic acid.

After 25 g of the obtained compound material B, 45 g ϵ -caprolactone polymer, and 930 g of a PBT resin ("Juranex" 2000, product of Polyplastics K.K.) were blended with a Henschel mixer, the obtained mixture was processed in the same way as described in Application Example 1. The properties of the obtained molding product were evaluated.

Application Example 5

100 g of swelling mica (cation-exchange capacity: 254 milliequivalents/100 g) were dispersed in 3 L water, followed by adding 102.4 g 12-aminododecanoic acid and 48.2 g of concentrated hydrochloric acid (concentration: 36%). The mixture was stirred at room temperature for 60 min. After being well rinsed, the mixture was filtered under reduced pressure using a Buchner funnel to obtain a water-containing compound material. The water-containing compound material was subjected to freeze-drying to synthesize a montmorillonite (compound material C) containing ammonium ions of 12-aminododecanoic acid.

After 25 g of the obtained compound material C, 0.25 g of a silane-based coupling agent (A-186, product of Nippon Unica K.K.), and 974.75 g of a PBT resin ("Juranex" 2000, product

of Polyplastics K.K.) were blended with a Henschel mixer, the obtained mixture was processed in the same way as described in Application Example 1. The properties of the obtained molding product were evaluated.

Application Example 6

100 g of synthetic saponite (cation-exchange capacity: 119 milliequivalents/100 g) were dispersed in 3 L water, followed by adding 51.2 g 12-aminododecanoic acid and 24.1 g of concentrated hydrochloric acid (concentration: 36%). The mixture was stirred at room temperature for 60 min. After being well rinsed, the mixture was filtered under reduced pressure by using a Buchner funnel to obtain a water-containing compound material. The water-containing compound material was subjected to freeze-drying to synthesize a montmorillonite (compound material D) containing ammonium ions of 12-aminododecanoic acid.

After 25 g of the obtained compound material D, 0.25 g of silane-based coupling agent (A-187, product of Nippon Unica K.K.), and 974.75 g of a PBT resin ("Juranex" 2000, product of Polyplastics K.K.) were blended with a Henschel mixer, the obtained mixture was processed in the same way as described in Application Example 1. The properties of the obtained molding product were evaluated.

Application Example 7

After 25 g of said compound material A, 42 g ϵ -caprolactone polymer, and 381.7 g 1,4-butanediol were fed into an autoclave equipped with a stirring device and were mixed uniformly in the system at 90°C, 703.8 g terephthalic acid and 2 g tetrabutyl titanate were added, followed by carrying out the polymerizing reaction using a conventional method. The obtained composite material contained 933 g PBT. The composite material was used to produce a molding product in the same way as described in Application Example 1. The properties of the obtained molding product were evaluated.

Comparative Example 1

A PBT resin ("Juranex" 2000, product of Polyplastics K.K.) was processed in the same way as described in Application Example 1, and the properties were evaluated.

Comparative Example 2

After 25 g montmorillonite produced in Yamagata Ken, 42 g ϵ -caprolactone polymer, and 933 g PBT resin ("Juranex" 2000, product of Polyplastics K.K.) were blended with a Henschel

mixer, the obtained mixture was processed in the same way as described in Application Example 1. The properties of the obtained molding product were evaluated.

Comparative Example 3

After 25 g of said compound material A and 975 g PBT resin ("Juranex" 2000, product of Polyplastics K.K.) were blended with a Henschel mixer, the obtained mixture was processed in the same way as described in Application Example 1. The properties of the obtained molding product were evaluated.

Comparative Example 4

After 25 g of glass fibers ("Glasron" JA429, product of Asahi Fiber Glass Co., Ltd.) and 975 g PBT resin ("Juranex" 2000, product of Polyplastics K.K.) were blended with a Henschel mixer, the obtained mixture was processed in the same way as described in Application Example 1. The properties of the obtained molding product were evaluated.

The results of Application Examples 1-7 and Comparative Examples 1-4 are listed in Table 1.

Table 1

No.	実 施 例 ①							対 照 例 ②			
	1	2	3	4	5	6	7	1	2	3	4
③	層状粘土鉱物の種類 (5)	12-Ti/FF 0.5g/1g	12-Ti/FF 0.5g/1g	12-Ti/FF 0.5g/1g	12-Ti/FF 0.5g/1g	12-Ti/FF 0.5g/1g	12-Ti/FF 0.5g/1g	12-Ti/FF 0.5g/1g	12-Ti/FF 0.5g/1g	12-Ti/FF 0.5g/1g	12-Ti/FF 0.5g/1g
	有機オニウムイオンの種類 (6)	12-Ti/FF 0.5g/1g	12-Ti/FF 0.5g/1g	12-Ti/FF 0.5g/1g	12-Ti/FF 0.5g/1g	12-Ti/FF 0.5g/1g	12-Ti/FF 0.5g/1g	12-Ti/FF 0.5g/1g	12-Ti/FF 0.5g/1g	12-Ti/FF 0.5g/1g	12-Ti/FF 0.5g/1g
	有機粘土鉱物の量(重量部) (7)	2.5	12.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
	相溶化剤の種類 (8)	0.5g/1g	0.5g/1g	0.5g/1g	0.5g/1g	0.5g/1g	0.5g/1g	0.5g/1g	0.5g/1g	0.5g/1g	0.5g/1g
④	相溶化剤の量(重量部) (9)	4.2	7.5	1.5	4.5	0.025	0.025	4.2	4.2		
	PBTの量(重量部) (10)	93.3	80	96	93	97.475	97.475	93.3	100	97.5	97.5
	引張強さ(GPa) (11)	1.07	1.35	1.28	1.41	1.34	1.24	1.15	0.99	1.03	1.10
	熱変形温度(°C) (12)	72	100	80	75	82	75	75	58	68	72
⑤	吸水率(%) (13)	0.70	0.28	0.50	0.65	0.50	0.60	0.54	1.43	1.31	1.25

- Key: 1 Application Example
 2 Comparative Example
 3 Composition
 4 Properties
 5 Type of layer clay mineral
 6 Type of organic onium ions
 7 Amount of organic clay mineral (parts by weight)
 8 Type of compatibilizer

9	Amount of compatibilizer (parts by weight)
10	Amount of PBT (parts by weight)
11	Tensile elastic modulus
12	Thermal deformation temperature
13	Water absorption rate
14	Montmorillonite
15	Swelling mica
16	Synthetic saponite
17	Glass fibers
18	12-Aminododecanoic acid
19	6-Aminocaproic acid
20	Poly- ϵ -caprolactone
21	PBT oligomer
22	Coupling agent A-186
23	Coupling agent A-187

Application Example 8

828 g terephthalic acid, 630 g ethylene glycol, 0.5 g calcium acetate, and 0.12 g antimony trioxide were fed into an autoclave equipped with a stirring device and were stirred at 197°C in nitrogen gas for 2 h. Then, after the system was kept at 220°C for 20 min, the reaction was carried out at 280°C for 1 h. The distilled water, methanol, and ethylene glycol were removed.

Then, the pressure in the reaction container was lowered to 0.1 mm Hg, and the reaction was continued until no more ethylene glycol was distilled. The number-average molecular weight of the polyethylene terephthalate (polymer E) as the obtained polymer was 25,000.

After 974.25 g of said polymer E, 25 g of said compound material A, and 0.25 g of a silane-based coupling agent (A-186, product of Nippon Unica K.K.) were blended with a Henschel mixer, the obtained mixture was extruded at 280°C. After that, a molding product was produced at a molding temperature of 280°C and a die temperature of 150°C. The properties of the molding product were evaluated. Also, the film formability at 280°C was evaluated.

Application Example 9

After 25 g of said compound material A, 42 g ϵ -caprolactone polymer, 0.25 g of a silane-based coupling agent (A-186, product of Nippon Unica K.K.), and 932.75 g of said polymer E were blended with a Henschel mixer, a molding product was produced in the same way as described in Application Example 8. The properties of the molding product were evaluated.

Application Example 10

After 25 g of said compound material B, 42 g ϵ -caprolactone polymer, and 933 g of said polymer E were blended with a Henschel mixer, a molding product was produced in the same way as described in Application Example 8. The properties of the molding product were evaluated.

Application Example 11

25 g of said compound material A, 42 g ϵ -caprolactone polymer, and 400 g ethylene oligomer were fed into an autoclave equipped with a stirring device and were mixed uniformly at 90°C in the system. Then, 0.6 g calcium acetate and 0.15 g antimony trioxide were added, followed by 2 h of stirring carried out at 198°C in nitrogen gas. Then, after the system was kept at 220°C for 30 min, the reaction was carried out at 280°C for 2 h. The distilled water, methanol, and ethylene glycol were removed.

Then, the pressure in the reaction container was lowered to 0.1 mm Hg, and the reaction was continued until no more ethylene glycol was distilled. The number-average molecular weight of the polyethylene terephthalate (933 g) as the obtained polymer was 22,000. The obtained polymer was used to form a molding product in the same way as described in Application Example 8. The properties of the obtained molding product were evaluated.

Comparative Example 5

Said polymer E was processed in the same way as described in Application Example 8 to form a molding product. The properties of the obtained molding product were evaluated.

Comparative Example 6

After 25 g of glass fibers ("Glasron" JA429, product of Asahi Fiber Glass Co., Ltd.) and 975 g of said polymer E were blended with a Henschel mixer, the mixture was processed in the same way as described in Application Example 8. The properties of the obtained molding product were evaluated.

Comparative Example 7

After 300 g of said compound material A, 1 g of a silane-based coupling agent (A-186, product of Nippon Unika K.K.), and 699 g of said polymer E were blended with a Henschel mixer, the mixture was processed in the same way as described in Application Example 8. The properties of the obtained molding product were evaluated.

The results of Application Examples 8-11 and Comparative Examples 5-7 are listed in Table 2.

Table 2

		(1) 実 施 例				(2) 比 較 例		
No		8	9	10	11	5	6	7
(4)	⑤ 層状粘土 鉱物の種類	モンモリ ロナイト	モンモリ ロナイト	モンモリ ロナイト	モンモリ ロナイト	(14)	カ1 蒙 性	モンモリ ロナイト (14)
	⑥ 有機オニウ ムイオンの種類	12-7-リ ン酸イオン	12-7-リ ン酸イオン	6-7-リ ン酸イオン	12-7-リ ン酸イオン	(16)		12-7-リ ン酸イオン (16)
	⑦ 有機粘土 鉱物の量 (重量部)	2.5 (16)	2.5 (19)	2.5 (17)	2.5		2.5	3.0
	⑧ 結合剤 の種類	おがく A-186 (18)	お-ε お おがく A-186	お-ε お おがく A-186 (20)	お-ε お おがく A-186 (20)			おがく A-186 (18)
(7)	⑨ 結合剤の 量 (重量部)	0.025	4.2 0.025	4.2	4.2			0.1
	⑩ PETの量 (重量部)	97.425	93.275	93.3	93.3	100	97.5	99.9
	⑪ 引張弾性 率 (GPa)	1.34	1.38	1.32	1.41	1.15	1.30	1.45
	⑫ 熱変形 温度 (°C)	89	92	91	91	78	90	102
(4)	⑬ 吸水率 (%)	0.51	0.34	0.81	0.48	1.35	1.05	0.50
	⑭ フィルム 成形性	○	○	○	○	×	×	×

- Key:
- 1 Application Example
 - 2 Comparative Example
 - 3 Composition
 - 4 Properties
 - 5 Type of layer clay mineral
 - 6 Type of organic onium ions
 - 7 Amount of organic clay mineral (parts by weight)
 - 8 Type of compatibilizer
 - 9 Amount of compatibilizer (parts by weight)
 - 10 Amount of PET (parts by weight)
 - 11 Tensile elastic modulus
 - 12 Thermal deformation temperature
 - 13 Water absorption rate
 - 14 Montmorillonite
 - 15 Glass fibers
 - 16 12-Aminododecanoic acid ions
 - 17 6-Aminocaproic acid ions
 - 18 Coupling agent A-186
 - 19 Poly-ε-caprolactone, coupling agent A-186
 - 20 Poly-ε-caprolactone
 - 21 Film formability

As can be seen from the aforementioned application examples and comparative examples, the composite material of the present invention has excellent total balance among

mechanical properties, thermal properties, and water resistance. The composite material can also be used as a film-forming material.

On the other hand, when glass fibers are blended, the mechanical properties and thermal properties can be improved. However, the water resistance is not well improved, and film formation is impossible.

When no compatibilizer is used, the mechanical properties and the thermal properties are not well improved. In particular, since the layer clay mineral is not uniformly dispersed, the water resistance is not well improved, and film formation is impossible. The same problems occur when using a layer clay mineral containing no organic onium ion.

If the amount of layer clay mineral containing organic onium ions used exceeds the prescribed level, film formation is also impossible due to aggregation of the layer clay mineral.